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## POLYSYNTHETIC TWINNING IN DOLOMITE<sup>1</sup>

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It is not generally known that polysynthetic twinning is fairly common in dolomite. No mention of it is made, for example, in such standard works as Dana's *System of Mineralogy* and Miers' *Mineralogy*. Some authors <sup>2,3</sup> go so far as to say that the absence of polysynthetic twinning in thin sections distinguishes dolomite from calcite. The purpose of this article is to show that polysynthetic twinning is common in dolomite and also to show that by means of this twinning, dolomite may often be distinguished from calcite since the twinning-law for dolomite is different from that for calcite.

Five different twinning-laws have been established for dolomite. They are as follows: (1) twinning-plane  $c(0001)$  or  $(111)$ ; (2) twinning-plane  $a(11\bar{2}0)$  or  $(101)$ ; (3) twinning-plane  $=m(10\bar{1}0)$  or  $(211)$ ; (4) twinning-plane  $=r(10\bar{1}1)$  or  $(100)$ ; (5) twinning-plane  $f(02\bar{2}1)$  or  $(11\bar{1})$ . Of these five twinning laws only the last one, as far as I can learn, is exemplified as polysynthetic twin-lamellae in dolomite. This type of twinning for dolomite was first described by Haidinger.<sup>4</sup> Since then it has been mentioned by Tschermak,<sup>5</sup> Leuze<sup>6</sup>, Vogt,<sup>7</sup> Grünling,<sup>8</sup> and Redlich.<sup>9</sup>

With this introduction I shall now proceed to the description of such polysynthetically-twinned dolomites as have come under my notice.

<sup>1</sup> Paper presented at the ninth annual meeting of the *Mineralogical Society of America*, New York, Dec. 28, 1928.

<sup>2</sup> Winchell, *Elements of Optical Mineralogy*, 1st. ed., p. 144, New York, 1909.

<sup>3</sup> Klockmann, *Lehrbuch der Mineralogie*, 7 and 8th ed., p. 457, Stuttgart, 1922.

<sup>4</sup> *Annalen der Physik und Chemie*, vol. 63, pp. 153-158, 1844.

<sup>5</sup> *Petr. u. Min. Mith.*, (Neue Folge) vol. 4, p. 108, 1882.

<sup>6</sup> *Ber. d. XXVII Versamml. d. Oberrhein. geol. Verein.*, p. 81, 1894.

<sup>7</sup> *Zeit. f. prakt. Geol.*, vol. 6, p. 11, 1898.

<sup>8</sup> *Zeit. f. Kryst. u. Min.*, vol. 33, p. 216, 1900.

<sup>9</sup> *Zeit. f. prakt. Geol.*, vol. 21, p. 412, 1913.

## DOLOMITE FROM THE TILLY FOSTER MINE, BREWSTER, N. Y.

My attention was first directed to polysynthetically-twinned dolomite in specimens collected by me at this famous mineral locality in 1908. The specimens are large grayish-white cleavage masses of dolomite up to 10 cm. in size associated with chlorite and chondrodite. The cleavages are usually regular and smooth, and more nearly resemble calcite than dolomite. The specific gravity of the mineral is 2.85 and since it contains both magnesium and calcium in large amounts, with a small amount of iron, it must be dolomite.

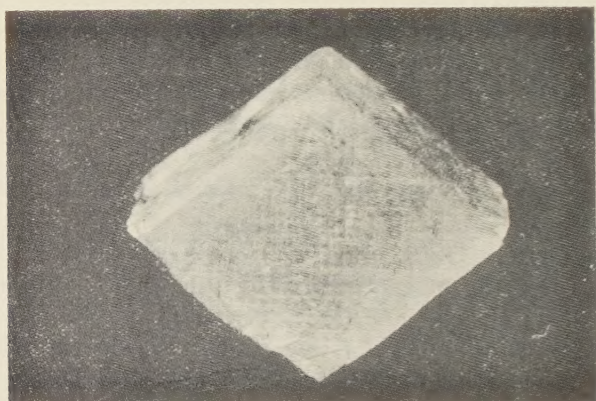


FIG. 1. (x3)—Cleavage rhombohedron of dolomite from the Tilly Foster Mine, N.Y., showing twin-striations. (weathered surface.)

On close examination, the cleavage surfaces of the dolomite show striations parallel to the short or long diagonals or sometimes both to short and long diagonals. Figure 1 shows the striations on a cleavage surface. Thin sections show conclusively that the apparent striations are thin twin-lamellae. With polysynthetic twinning parallel to  $(02\bar{2}1)$  the striations appear parallel to the short diagonal on two faces and parallel to the long diagonal on one face, as shown in Fig. 3. It will be recalled that the unit positive rhombohedron  $(10\bar{1}1)$  truncates the polar edges of the negative rhombohedron  $(02\bar{2}1)$ . (For comparison calcite with twinning parallel to  $(01\bar{1}2)$  is shown in Fig. 2). Now the explanation of the variation in the position of the lamellae is that the twinning may be parallel

to either one, two, or three faces of the rhombohedron. The drawings of Figs. 5, 6, and 7 bring this out very clearly. Each of these three cases has actually been observed. If it is assumed that the three styles of twinning are equally common, the ratio between the

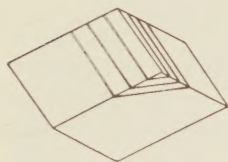


FIG. 2.—Calcite cleavage rhombohedron with polysynthetic twinning parallel to  $(01\bar{1}2)$ .

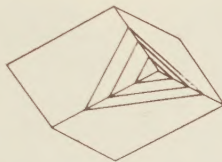


FIG. 3.—Dolomite cleavage rhombohedron with polysynthetic twinning parallel to  $(02\bar{2}1)$ .

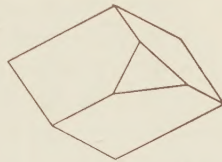
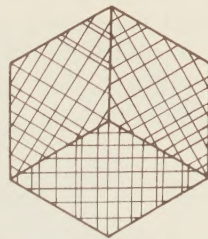
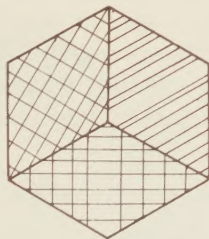
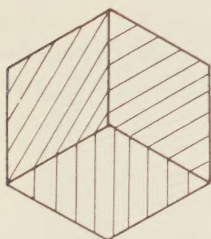


FIG. 4.—Dolomite cleavage rhombohedron with parting parallel to  $f(20\bar{2}1)$ , which is due to twinning.

occurrence of striations, parallel to short diagonal, long diagonal, and both diagonals is as 3:1:5.

Some specimens of the dolomite show a well-defined parting parallel to  $(02\bar{2}1)$  as illustrated in Fig. 4. The angle  $r(10\bar{1}1):f(02\bar{2}1)$  on measurement gave  $50^{\circ}15'$  (average of 10 measurements varying from  $49^{\circ}$  to  $51\frac{1}{2}^{\circ}$ ) as against the calculated value  $50^{\circ}12'$ .

In thin sections this parting is also occasionally observed. The parting surfaces, which are dull in contrast with lustrous cleavage



Plans of the cleavage rhombohedron of dolomite showing polysynthetic twinning parallel to

FIG. 5.—One face  $(02\bar{2}1)$  FIG. 6.—Two faces:  $(02\bar{2}1)$  and  $(\bar{2}021)$  FIG. 7.—Three faces  $(02\bar{2}1)$ ,  $(20\bar{2}1)$ , and  $(\bar{2}021)$ .

faces, range up to 4 cm. None of the text-books or treatises make any mention of the parting. The parting is clearly the result of winning.

In thin sections cut parallel to the cleavage, twin-lamellae parallel both to the short and long diagonals are observed. The width of



the lamellae parallel to the short diagonal varies from 0.015 to 0.075 mm. As many as 50 lamellae may be counted in a space of 1 cm. Many of the lamellae are so thin that they show first order interference colors instead of the high order colors of the main part of the section.

Some specimens of the Tilly Foster dolomite show an irregular penetration twinning parallel to (0001) in addition to polysynthetic twinning parallel to (02 $\bar{2}$ 1). This twinning is recognized by the fact that the cleavage surfaces of the two individual members of the twin are in the same vertical zone [0001].

#### DOLOMITE FROM PROVIDENCE, RHODE ISLAND

A pure white cleavable dolomite associated with pale green talc from this locality, which was obtained from Ward's Natural Science Establishment, also shows polysynthetic twinning with the twin-plane  $f(02\bar{2}1)$ . In addition there is also penetration twinning with  $c(0001)$  as the twin-plane. A detailed description of this dolomite would closely parallel that of the Tilly Foster dolomite except for the absence of parting and the difference in associated minerals. This mineral also greatly resembles calcite, but the polysynthetic twinning distinguishes it from that mineral at sight. The determination was confirmed by qualitative chemical tests for calcium and magnesium and by a specific gravity determination which gave 2.88. Fig. 8 is a photomicrograph showing twinning lamellae parallel both to the short and long diagonals. The lamellae parallel to the short diagonal are about 0.05 mm. wide.

#### DOLOMITE FROM CHARLEMONT, MASS.

Euhedral iron-bearing dolomite (ankerite) crystals from  $\frac{1}{2}$  cm. to  $1\frac{1}{2}$  cm. in size, embedded in a talc-chlorite schist which occurs near Charlemont, Mass., show polysynthetic twinning parallel to (02 $\bar{2}$ 1) on cleavage surfaces. Except where inclusions are abundant the crystals (positive unit rhombohedra) are colorless, but on a weathered surface they are brownish.

A photomicrograph (see Fig. 9) of a thin section oriented parallel to (10 $\bar{1}$ 1) shows numerous twin-lamellae parallel to the short diagonal. In this occurrence the lamellae are about 0.05 mm. wide.

## DOLOMITE FROM FOREIGN LOCALITIES

Several specimens of white cleavable dolomite from Moravia (the exact locality is not known) show narrow, but well defined

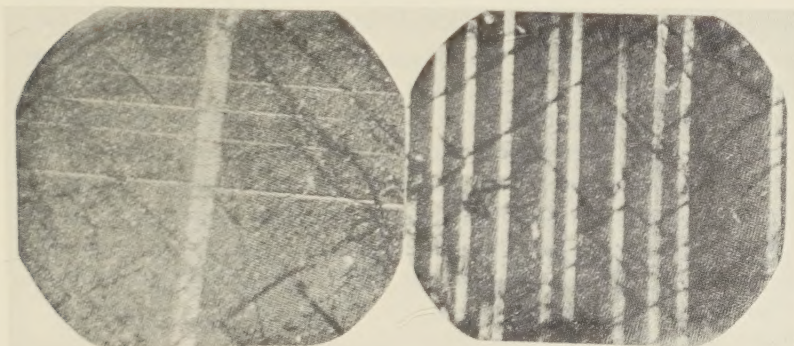


FIG. 8. (x57) Twin-lamellae in dolomite from Providence, R. I., Nicols crossed. The broad lamella is parallel to the short diagonal and the narrow lamellae, parallel to the long diagonal.

FIG. 9. (x24) Twin-lamellae in dolomite parallel to the short diagonal. Nicols crossed. Charlemont, Mass.

twin-lamellae parallel both to the short and long diagonals. These are large pieces with flat cleavage surfaces up to 6 by 8 cm. One specimen shows a small parting surface parallel to  $(02\bar{2}1)$ . They



FIG. 10. (x8). Thin section of metamorphic dolomite rock from Tuckahoe, N. Y., showing twin lamellae parallel to the short diagonal.

FIG. 11. (x8) The same with crossed nicols.

resemble calcite at first sight and are very much like the Tilly Foster and Providence specimens.

Cleavable ferriferous dolomite (ankerite) from Eisenerz, Styria, in our collections also shows on close examination numerous fine twin-lamellae parallel to both short and long diagonals.

#### METAMORPHIC DOLOMITE ROCKS

On careful examination, the cleavage surfaces of the mineral grains of the metamorphic dolomites from the upper part of New York City, Tuckahoe, N. Y., Ossining, N. Y., Amity, N. Y., Salinas, Cal., near Hollister Cal., and several unknown localities show these twin-striations. The photomicrographs of Figs. 10 and 11 (from a specimen from Tuckahoe, N. Y.) give a good idea of the appearance of the twin-lamellae in thin sections. They are as well marked as the twin-lamellae in calcite grains of metamorphic limestones.

#### PETROGRAPHIC IMPORTANCE OF POLYSYNTHETIC TWINNING IN DOLOMITE

The wide-spread prevalence of lamellar twinning parallel to (02 $\bar{2}$ 1) in metamorphic dolomite rocks gives this method of twinning a petrographic as well as a mineralogic importance. The presence of twin-lamellae furnishes us a good method of distinguishing dolomite from calcite. I have never found any of the polysynthetic twinning in the dolomite of sedimentary rocks. This fact makes it probable that the twinning is the result of pressure.



# THE PREPARATION OF PROJECTION DIAGRAMS

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In crystallographical, optical, and X-ray work with crystals, projection diagrams of several different types are widely used, especially for the graphical analysis of data of measurement. In crystallography, the gnomonic and stereographic projection plots serve the purpose best; in crystal optics, the stereographic, the

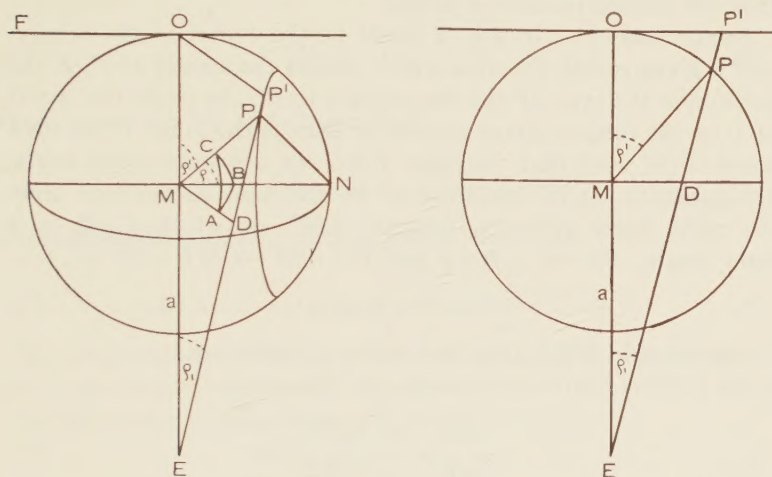


Fig. 1

Diagram used in the derivation of the formula for parallels of latitude in perspective projection diagrams. The point  $E$  is the eye of the observer;  $P$ , the point on the sphere projected to  $P'$  on the plane  $FOP'$ , tangent to the sphere at  $O$ , or to  $D$  on the equatorial plane  $NMD$  normal to  $EM$ . The angle  $NMP = \rho$ ,  $OMP = \rho'$ ,  $NMD = \phi$ .

Fig. 1a

The plane  $EOP'$  of Fig. 1 drawn in the plane of the paper to show the angular relations.

orthographic, and the angle projection plots; in X-ray analysis, the reflection and the gnomonic projections. The preparation of these projection plots, which represent the sphere with its parallels of latitude and meridians of longitude, spaced either  $1^\circ$  or  $2^\circ$  apart is a tedious task; but once drawn, they can be reproduced and made available by publication. This has been done for the more important projections and the diagrams or nets have long been in use. It is of interest, however, to derive and to list the equations

that form the basis for these projection plots and to compare the several projections from this viewpoint.

**THE PERSPECTIVE PROJECTIONS.** In these projections the eye of the observer is located at a definite point in space from which the points on the surface of the sphere are viewed. The points of intersection of the lines of sight with the fixed plane of projection are then the desired projection points.

**SMALL CIRCLES.** In Fig. 1 let  $M$  be the center of the sphere,  $MP$  a given radial direction which pierces the sphere at  $P$ ,  $E$  the position of the eye,  $EP$  the line of sight to  $P'$ , the projection point of  $P$  on the tangent plane normal to  $EO$ . If the point  $P$  lies on a small circle, such that the angle  $PMN = \rho$ , a definite given angle, an expression for the condition to be met can be deduced from the right angle spherical triangle  $ABC$ , in which  $CAB$  is a right angle,  $BA = \phi$ ,  $CB = \rho$  and  $CA = 90^\circ - OMP = 90 - \rho^1$ ,

$$\cos \rho = \cos \phi \cdot \sin \rho^1. \quad (1)$$

In the triangle  $MEP$ , (Fig. 1a)  $MP = 1$ ,  $ME = a$  and angle  $MPE = PMO - PEM = \rho^1 - \rho_1$ . Therefore

$$\frac{ME}{MP} = \frac{\sin MPE}{\sin MEP} \quad \text{or}$$

$$a = \frac{\sin (\rho^1 - \rho_1)}{\sin \rho_1} = \sin \rho^1 \cdot \cot \rho_1 - \cos \rho^1. \quad (2)$$

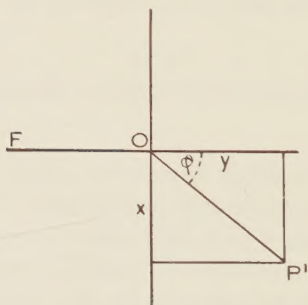


Fig. 1b

Diagram to show the relations in the projection plane  $FOP'$  of Fig. 1.

In the tangent plane of projection, the line  $OP' = (1 + a) \cdot \tan \rho_1$  and (Fig 1b)



$$x = (1+a) \tan \rho_1 \cdot \sin \phi$$

$$y = (1+a) \tan \rho_1 \cdot \cos \phi$$

Therefore

$$\cos \phi = \frac{y}{\sqrt{x^2 + y^2}} \quad (3)$$

$$\tan \rho_1 = \frac{\sqrt{x^2 + y^2}}{1+a} \quad (4)$$

From equations (1) and (2) we find

$$\cos \rho \cdot \cot \rho_1 = a \cos \phi + \sqrt{\cos^2 \phi - \cos^2 \rho} \quad (5)$$

Combining this equation with (3) and (4) we obtain

$$(1+a) \cos \rho - ay = \sqrt{y^2 - \cos^2 \rho \cdot (x^2 + y^2)} \quad (6)$$

By assigning to  $a$  different values we ascertain for each perspective projection its appropriate equation.

In the *gnomonic* projection  $a = 0$ , and (6) reduces to

$$y^2 = \cot^2 \rho \cdot (1 + x^2) \quad (6a)$$

the equation of an hyperbola.

In the *orthographic* projection  $a = \infty$  and (6) becomes

$$y = \cos \rho \quad (6b)$$

the equation of a straight line.

In the *stereographic* projection  $a = 1$ ; the projection plane, is, moreover, the equatorial plane and the coordinates  $x'$ ,  $y'$  are half the normal values. Equation (6) reduces to

$$\cos \rho \cdot (4 + x^2 + y^2) = 4y, \quad \text{or} \quad \cos \rho \cdot (1 + x'^2 + y'^2) = 2y' \quad (6c)$$

or

$$\left( y' - \frac{1}{\cos^2 \rho} \right)^2 + x'^2 = \tan^2 \rho$$

the equation of a circle.

**GREAT CIRCLES.** In Fig. 2 let  $LPKN$  be a great circle, the plane of which includes the angle  $KMO = \rho$  with the pole  $MO$ . Let  $P$  be a point on the great circle that is to be plotted in projection. In

the spherical triangle  $POK$ ,  $OK = \rho$ ,  $OP = \rho^1$ ,  $KOP = \phi$ , and  $PKO = 90^\circ$ .

Therefore

$$\tan \rho = \cos \phi \tan \rho^1 \quad (7)$$

In triangle  $PMO$  equation (2) applies as heretofore

$$a = \frac{\sin(\rho^1 - \rho_1)}{\sin \rho_1} = \sin \rho^1 \cdot \cot \rho_1 - \cos \rho^1 \quad (2)$$

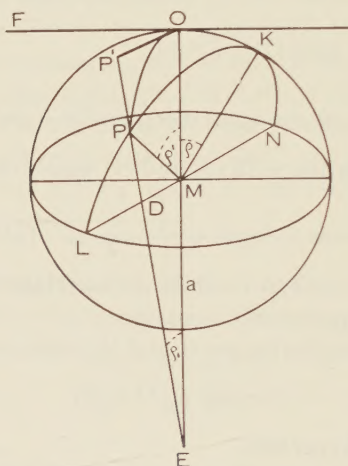


Fig. 2

Diagram used in the derivation of the formula for great circles in perspective projection. The point  $E$  is the eye of the observer;  $P'$  and  $D$  are the projection points of  $P$  respectively on the tangent and equatorial planes, normal to  $EM$ .

Combining (2) and (7) to eliminate  $\rho^1$  we find,

$$a\sqrt{\tan^2 \rho + \cos^2 \phi} = \tan \rho \cdot \cot \rho_1 - \cos \phi$$

and this equation together with (3) and (4) yields

$$(a+1) \cdot \tan \rho - y = a\sqrt{y^2 + \tan^2 \rho \cdot (x^2 + y^2)}. \quad (8)$$

By assigning proper values of  $a$  for the several projections we find for the different projections:

*Gnomonic* projection.  $a = 0$

$$y = \tan \rho \quad (8a)$$

the equation of a straight line.

*Orothographic* projection.  $a = \infty$

$$\frac{y^2}{\sin^2 \rho} + x^2 = 1 \quad (8b)$$

the equation of an ellipse.

*Stereographic* projection. Projection plane is the equatorial plane and coordinates  $x'$ ,  $y'$  are half the normal values;  $a = 1$

$$(y + 2 \cot \rho)^2 + x^2 = \frac{4}{\sin^2 \rho}$$

or

$$(y' + \cot \rho)^2 + x'^2 = \frac{1}{\sin^2 \rho} \quad (8c)$$

the equation of a circle.

#### THE REFLECTION PROJECTION

This is the projection in which the points of the diffraction pattern in the X-ray photograph of a single crystal appear. This projection bears the same relation to the gnomonic projection that the gnomonic projection bears to the stereographic. In each case, the azimuth angles,  $\phi$ , remain the same; as  $\rho$  is the angle between the pole and the direction represented by the point in the projection, the distance of the point in projection from the pole is  $\tan \rho/2$  in the *stereographic* projection,  $\tan \rho$  in the *gnomonic*, and  $\tan 2\rho$  in the *reflection* projection. The relations are illustrated in Fig. 3.

The equations for the small and great circles of the reflection projection plot are ascertained by the methods noted above.

*Small circles.* Equation(1)

$$\cos \rho = \cos \phi \cdot \sin \rho^1 \quad (1)$$

is valid as heretofore. Also in the projection plane we have

$$x = \tan 2\rho^1 \cdot \sin \phi$$

$$y = \tan 2\rho^1 \cdot \cos \phi$$



$$\cos \phi = \frac{y}{\sqrt{x^2 + y^2}} \quad (9)$$

$$\tan 2\rho^1 = \sqrt{x^2 + y^2} \quad (10)$$

By combining equations 1, 9, and 10, we obtain the expression

$$y^4 = 4 \cos^2 \rho \cdot (1 + x^2 + y^2) [y^2 - \cos^2 \rho \cdot (x^2 + y^2)] \quad (11)$$

which represents a curve of the fourth degree.

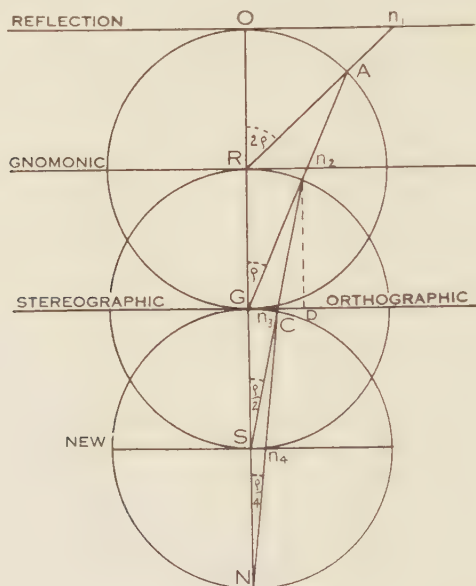


Fig. 3

Sectional diagram to illustrate the relations between the different projections listed.

*Great circles.* Equation (7)

$$\tan \rho = \cos \phi \cdot \tan \rho^1 \quad (7)$$

combined with equations 9 and 10 yields the expression for the great circle curves in this projection

$$y^2(1 - \tan^2 \rho) - \tan^2 \rho \cdot x^2 = 2y \tan \rho \quad (12)$$

or

$$(2 \cot 2\rho \cdot y - 1)^2 - (1 - \tan^2 \rho) x^2 = 1 \quad (12a)$$

This is the equation of an hyperbola for angles  $\rho < 45^\circ$ .

*A new projection.* If Fig. 3 were extended downward to include a third sphere a new projection would result that bears the same relation to the stereographic that the stereographic does to the gnomonic. It is not difficult to write down the equations for the great and small circles in this projection which projects the entire sphere within a circle of unit radius.

*Small circles.* For these circles on the sphere the relation expressed by equation 1 is valid

$$\cos \rho = \cos \phi \sin \rho^1. \quad (1)$$

Also the equations

$$x = \tan \frac{\rho}{4} \cdot \sin \phi$$

$$y = \tan \frac{\rho}{4} \cdot \cos \phi$$

$$\cos \phi = \frac{y}{\sqrt{x^2 + y^2}} \quad (13)$$

$$\tan \frac{\rho^1}{4} = \sqrt{x^2 + y^2} \quad (14)$$

From equations 1, 13, and 14 the expression can be deduced

$$(1 + x^2 + y^2)^2 \cos \rho = 4y(1 - x^2 - y^2) \quad (15)$$

which represents a curve of the fourth degree.

*Great circles.* From equation 7

$$\tan \rho = \cos \phi \cdot \tan \rho^1 \quad (7)$$

and from equations 13 and 14 we find the expression

$$(1 - x^2 - y^2)^2 - 4(x^2 + y^2) = 4 \cdot \cot \rho \cdot y(1 - x^2 - y^2) \quad (16)$$

which represents a curve of the fourth degree.

These equations are more complex than those of the foregoing projections. The projection is neither angle true nor area true and will be useful only rarely, where it is desired to project the major part of a sphere. It is, however, like the foregoing projections a type of perspective projection.

The new projection serves to project the entire sphere within a circle of unit radius. The stereographic projection represents the hemisphere in a circle of unit radius, and the whole sphere if the plane of projection is indefinitely extended. It is angle true; all zone lines are circular arcs. The gnomonic projection represents the hemisphere on a plane extending to infinity in all directions. On it all zone lines are straight lines. The reflection projection represents a spherical cone of  $45^\circ$ , if the plane of projection is indefinitely extended.



# AN ARTIFICIAL GEM-STONE ISOMORPHOUS WITH SPINEL

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## INTRODUCTION<sup>1</sup>

Two crystalline types of artificial gem-stones are now manufactured on a commercial scale. From the chemical standpoint these are either alumina or magnesium-aluminate. The alumina type (artificial corundum) has been manufactured in several different colors for some time.<sup>2</sup> Magnesium-aluminate gem-stones, however, have only recently assumed commercial importance in the artificial gem trade.

According to Clarke the magnesium-aluminate, spinel, has been synthesized in several ways and by a number of investigators.<sup>3</sup> It has also been known for some time that gem material approaching spinel in character can be manufactured. Smith<sup>4</sup> described artificial gem-stones which he called synthetic spinel over twenty years ago. These had the physical properties of spinel and agreed both in optical properties and system of crystallization with that mineral. No chemical analysis, however, was included in his description and it is not certain how the product corresponded with spinel.

Recently Rinne has carried out an extended study of synthetic spinel.<sup>5</sup> His work leaves little to be added to the subject. It seems proper, however, to give a few observations which may be of interest to readers of the *American Mineralogist*, although the work has not been carried out with the refinement accomplished by Rinne and his assistants. In view of the fact, however, that only slight attention has been paid to synthetic spinel by American writ-

<sup>1</sup> The artificial gem-stones studied in this investigation were kindly furnished by Mr. Milton Heller of L. Heller and Son.

<sup>2</sup> Verneuil, A., *Memoire sur la reproduction artificielle du rubis par fusion. Ann. d. ch. et de phys.*, S. 8, 3, 1904, p. 20.

<sup>3</sup> Clarke, F. W., *Data of Geochemistry*, 5th ed., *Bull.* 770, *U. S. Geol. Surv.*, 1924.

<sup>4</sup> Smith, G. F. Herbert, Note on synthetical corundum and spinel. *Mineral. Mag.*, 15, 1908, p. 153.

<sup>5</sup> F. Rinne, *Morph. u. phys.-chem. Untersuchungen an synthetischen Spinelten*, etc., *Neues Jahrb. Min., Geol.*, LVIII. Beilage-Band. Abt. A. Erstes Heft, 1928, pp. 43-108.

ers, it would seem that it should not be amiss to make available some independent observations on commercial material now being handled in this country.

An opportunity was recently offered the writer to examine several packets of artificial gems. The stones were of three colors, pale blue, bluish green, and rose-pink, and presented a most striking appearance. Upon examination and analysis all proved to be composed of the same substance. This substance was essentially a magnesium-aluminate isomorphous with spinel.



FIG. 1. "Boules" of artificial gem-stones now on the market. The three lower ones represent a magnesium-aluminate type, while the upper "boule" is synthetic corundum.

#### THE PROPERTIES OF THE ARTIFICIAL GEM-STONES

The stones are formed by the same blowpipe method employed in producing artificial corundum gems. The "boule," as the uncut material is called, grows upward by the addition of fused matter from the mouth of an oxy-hydrogen blowpipe mounted in a vertical position. The final product has the shape of the lower specimens shown in Figure 1. A "boule" formed of the more commonly known alumina, on the other hand, grows into a rounded, more or less pear-shaped form, as illustrated in the upper central part of the

figure. The magnesium-aluminate "boules" may be well crystallized. Occasionally a crystal resembling the usual spinel twin results from the fusion. More often, however, the cross section is nearly square. Partly developed octahedral forms are common. Cubic parting is evident in some specimens, and in others the stone breaks along octahedral planes.

The hardness of the material is 8. The specific gravities of the three stones were determined as follows:

Pale blue	3.71
Bluish-green	3.57
Rose pink	3.48

The index of refraction varies little from stone to stone, being very nearly  $N_{Na}$  equals 1.721. This is slightly greater than the figure given by Melczer,  $N_{Na}$  equals 1.7188 for blue spinel from Ceylon.<sup>6</sup> The material is in general isotropic but shows weak double refraction forming a gridlike pattern. This was noted by Michel,<sup>7</sup> and is given by him as a criterion for the recognition of stones which he calls "synthetic spinel." Judging from the work of those who have investigated the magnesia-alumina series,<sup>8</sup> the double refraction may indicate the presence of an additional  $Al_2O_3$  phase with the phase  $Mg\ Al_2O_4$ . The question of this phase is taken up in detail by Rinne.<sup>9</sup>

The properties of these artificial gem-stones differ considerably from those of the artificial corundum gems.<sup>10</sup> The difference is so distinct that no occasion should arise for confusing them with the other product.

#### AN X-RAY STUDY OF THE GEM-STONES

X-ray diffraction patterns were taken of both the pink artificial gem-stone and ruby spinel from Ceylon. These were measured and the interplanar atomic spacings computed. A comparison of the results of the two sets of computations is shown by diagram in Figure 2. The artificial product is evidently isomorphous with the Ceylon spinel, but the interplanar spacings are smaller than in the mineral.

<sup>6</sup> Melczer, G., Ueber einige Mineralien, vorwiegend von Ceylon. *Zeit. Krist.*, **33**, 1900, p. 259.

<sup>7</sup> Michel, H., The Pocketbook for Jewelers. Gustave Herz, New York, 1928.

<sup>8</sup> Rankin, G. A., and Merwin, H. E., The Ternary System  $CaO-Al_2O_3-MgO$ , *Journ. Amer. Chem. Soc.*, **38**, 1916, p. 571.

<sup>9</sup> *Loc. cit.*

<sup>10</sup> Moses, A. J., Some Tests upon the Synthetic Sapphires of Verneuil. *Amer. Journ. Sci.*, **30**, 1910, p. 271.



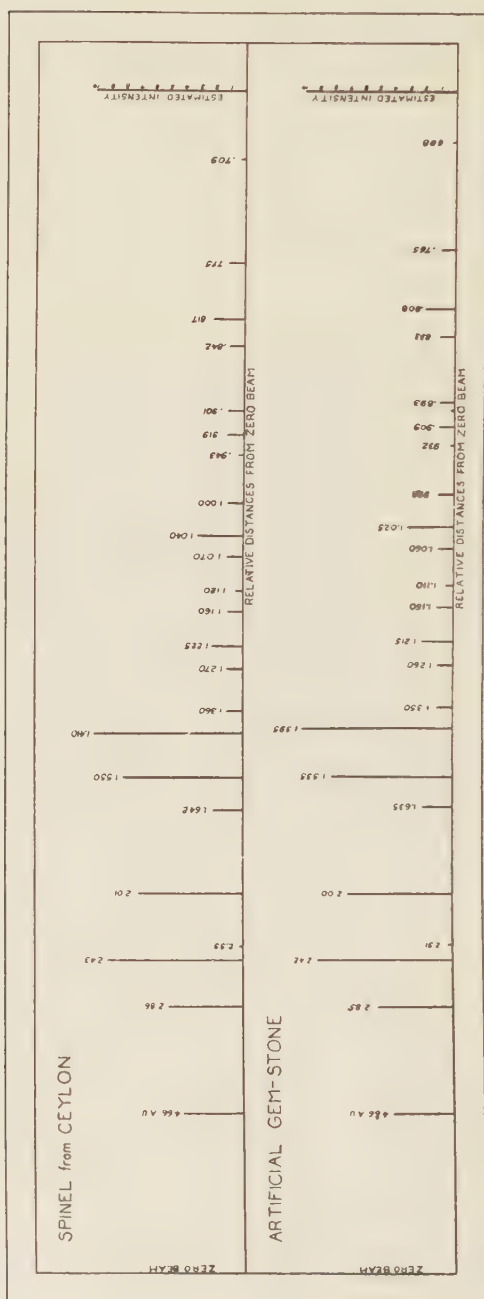


Fig. 2 Diagram giving the relative interplanar atomic spacing of Ceylon spinel and the artificial gem-stone of the spinel type. The lines show the relative distance from the zero beam as measured on an X-ray diffraction pattern, the estimated intensity of lines, and the interplanar atomic spacing in Angstrom units.

The crystal structure of the spinel group has been investigated by Bragg,<sup>11</sup> Nishikawa,<sup>12</sup> and Goldschmidt.<sup>13</sup> These authors agree in assigning the diamond type of lattice to the group and the spinel structure which they determined has since become a standard type. The spinel mineral examined by Nishikawa was ruby spinel from Ceylon. Judging from the description it was of the same type as that used for comparison in Figure 2. It may be assumed, therefore, that the diffraction pattern of the Ceylon material is that to be expected from a crystal having the diamond type of lattice and the atomic arrangement of spinel. The artificial product would also be made up of atoms arranged according to the "spinel type" of structure. In the latter case, however, the interplanar spacing is less. Computation of the Miller indices of the lines given by the artificial stone according to the method of Hull,<sup>14</sup> shows the material to have the generally recognized "spinel type" of structure. Posnjak,<sup>15</sup> has worked out the lattice dimensions of spinel by means of X-ray diffraction patterns and has given detailed measurements.

According to Bragg, the distance  $2d(100)$  for magnetite is 4.15 Å. U. In the case of the Ceylon spinel shown in Figure 2, the distance  $2d_{100}$  is 4.02 Å. U. and the same spacing for the artificial gem-stones is 4.00 Å. U. The difference between 4.00 Å. U. and 4.15 Å. U. probably very nearly represents the range of  $2d_{100}$  for the spinel group, for in other X-ray work it has been shown that<sup>16</sup> franklinite is at least close to magnetite and possibly the same, while chromite lies between magnetite and spinel.

#### CHEMICAL ANALYSIS

The magnesia content of the three samples tested was shown by analysis to be too low for ruby spinel.<sup>17</sup> The alumina content was

<sup>11</sup> Bragg, W. H., The structure of the Spinel Group of Crystals. *Phil. Mag.* 30, 1915, p. 305.

<sup>12</sup> Nishikawa, S., *Proc. Tokyo Math. Phys. Soc.*, 8, 1915-16, p. 199.

<sup>13</sup> V. M. Goldschmidt, T. Barth u. G. Lunde, *Norsk Vidensk.-Akad.*, Oslo, Mat.-naturv. Kl., 1925, N. F. I.

<sup>14</sup> Hull, A. W., A New Method of X-ray Crystal Analysis, *Phys. Rev.*, 10, 1917, p. 661.

<sup>15</sup> Posnjak, E., *Amer. J. Sci.*, Ser. 5, vol. XVI, 1928, p. 528.

<sup>16</sup> Kerr, Paul F., The determination of opaque ore-minerals by X-ray diffraction patterns. *Econ. Geol.*, 19, 1924, p. 1.

<sup>17</sup> All of the chemical work was carried on by Ledoux & Co., New York, under the supervision of Mr. A. M. Smoot.

correspondingly too high. The results of the two partial analyses and a portion of a complete analysis of the rose-pink colored stone are as follows:

	ROSE-PINK STONE	BLUISH-GREEN STONE	BLUE STONE
Alumina ( $\text{Al}_2\text{O}_3$ )	87.50%	89.17%	88.95%
Magnesia ( $\text{MgO}$ )	10.66%	9.69%	9.70%
		98.86%	98.65%

Crystals of pale ruby spinel from Ceylon were carefully selected and submitted for a complete analysis, to be compared with a complete analysis of the rose-pink artificial stone. The results of these two analyses are given below:

	RUBY SPINEL FROM CEYLON	ROSE-PINK ARTIFICIAL GEM-STONE
Alumina ( $\text{Al}_2\text{O}_3$ )	70.00 per cent	87.50 per cent
Magnesia ( $\text{MgO}$ )	28.10 " "	10.66 " "
Calcium oxide ( $\text{CaO}$ )	0.06 " "	0.06 " "
Ferrous oxide ( $\text{FeO}$ )	0.45 " "	0.82 " "
Chromic oxide ( $\text{Cr}_2\text{O}_3$ )	0.39 " "	not found
Silica ( $\text{SiO}_2$ )	0.74 " "	0.62 " "
Titanium oxide ( $\text{TiO}_2$ )	0.10 " "	not found
Manganese oxide ( $\text{MnO}$ )	trace	trace
	99.84 per cent	99.66 per cent

The analysis of the spinel from Ceylon agrees closely with other analyses of spinel from the same locality already on record. It is also not far from the theoretical composition of spinel. The magnesia and alumina content of the rose-pink artificial gem-stone, however, differ considerably from spinel. The material, therefore, is properly a synthetic isomorph of spinel.

#### CONCLUSION

The artificial gem-stones, as has been previously recognized, have the crystal structure of spinel. The atomic spacing based on X-ray patterns, however, is  $2d_{100}$  4.00 Å. U., instead of  $2d_{100}$  4.02 Å. U. as in the case of ruby spinel. The magnesia content of the material is also much too low to agree with ruby spinel, while the alumina on the other hand is correspondingly high. The optical and physical properties, however, agree closely with those of spinel, and it is, therefore, concluded that the material is a synthetic isomorph of spinel. Rinne has shown, however, that synthetic spinel with the correct magnesia-alumina ratio can be manufactured.

# BASE EXCHANGE IN ARTIFICIAL AUTUNITES.<sup>a</sup>

J. G. FAIRCHILD, *U. S. Geological Survey.*

## INTRODUCTION

By W. T. SCHALLER

Some years ago, while relating to Prof. A. N. Winchell, of Madison, Wisconsin, the results of readily hydrating and dehydrating autunite with the formation of definite hydrates with characteristic optical properties,<sup>1</sup> he raised the question as to whether or not the calcium in autunite could be replaced by other bases, with similar ease. Mr. J. G. Fairchild was at that time making artificial pyromorphite by a "salting out process" and kindly undertook the problem of making artificial autunite by the same process. Using sodium chloride as the "salting out" reagent, a well crystallized product was obtained, which to our surprise was found on analysis to contain only a little calcium and much sodium. As such a result strongly indicated that the base exchange reaction, as suggested by Winchell, was feasible, Fairchild agreed to undertake the necessary laboratory work and analysis, and to find out whether or not the calcium in autunite could be readily replaced by other bases. As both the calcium and the sodium artificial autunites could be prepared in quantity with ease, all the work was done on such artificial material.

The results, given below, show that such base replacement takes place very readily and that a large number of such different artificial autunites can be made. Starting with an artificial calcium autunite, all the calcium was readily replaced by sodium; starting with an artificial sodium autunite, the sodium was readily replaced by calcium, potassium, barium, manganese, copper, nickel, lead, and magnesium. With lead the end product was neither homogeneous nor well crystallized and the lead percentage was too high. A lead autunite was, however, successfully made by another method.

These experiments show that base exchange reactions take place very readily with compounds of the autunite type. All of the products obtained, with the exception of the lead-containing replacement product, were tetragonal plates four or eight sided, both uniaxial and biaxial, which had values for the refractive indices concordant with those found for the corresponding natural minerals.

Like so much of the natural autunite, some plates were isotropic when lying flat and birefringent when turned up on edge, whereas other plates showed a weak and irregular birefringence in the basal plates. No quantitative refractive index measurements were made consistently on any of these samples at the time they were analyzed; neither were they determined where the material was under known hygroscopic control. In fact most of the determinations were made several years after the material was analyzed but on material from the same tube from which the sample analyzed was obtained. A few check determinations, however, showed that no material change in the water content of the samples had taken place.

Like the natural autunites and other minerals of this same group, all the artificial preparations were optically unhomogeneous, a result probably due to the

<sup>a</sup> Published by permission of the Director, U. S. Geological Survey.

<sup>1</sup> The paper giving these results is in course of preparation.



presence of more than one hydrate in the sample.<sup>2</sup> The following optical varieties have been noticed in the artificial preparations, often all in one sample, and frequently several varieties form parts of a single crystal.

- (1) Strictly isotropic basal plates, uniaxial, negative.
- (2) Biaxial, weakly birefringent on basal plates.
- (3) Biaxial, strongly birefringent on basal plates.
- (4) Polysynthetically twinned, the lamellae being parallel to (100), or (110); or both.

The value of the axial angle also varied considerably on different crystals of the same sample.

#### METHODS OF PREPARATION

Several attempts were made to prepare artificial autunite in distinct crystals. The first attempt was made by boiling a solution of the nitrates of uranium and calcium with a solution of phosphoric acid. The resulting product was very fine-grained and apparently not homogeneous. The time element was then introduced and it was found that a well crystallized product could be obtained in a month or so by allowing a solution of uranium and calcium nitrate to mix very slowly with phosphoric acid by diffusion through a large volume of water. The first precipitate formed had an amorphous appearance but by leaving it undisturbed for a month or more, relatively large sized plates of well crystallized artificial autunite were obtained. While awaiting the outcome of this procedure, the method suggested by McDonnell and Smith<sup>3</sup> was employed, namely of precipitating the desired compound by a "salting out" process, using a strong solution of sodium chloride. Quite unexpectedly, the resultant crystals of artificial autunite, when analyzed, showed only about one-sixth of the required quantity of calcium. Tests soon showed that considerable sodium was present and quantitative analysis showed that these crystals were essentially the sodium equivalent of the calcium-uranium-phosphate.

In this "salting out" process, the action of the sodium chloride brine may be twofold; first, a reduction of the hydrolytic effect

<sup>2</sup> A study (unpublished) of natural autunite has shown that the variation in optical properties of autunites and the apparent inconsistency of their optical character as related to the geometrical form, is due chiefly to the existence of several hydrates whose stability range (at room temperature) is dependent on the vapor pressure of the surrounding air.

<sup>3</sup> McDonnell, C. C., and Smith, C. M., The preparation and properties of lead-chlor-arsenate, artificial mimetite. *Am. J. Sci.*, 4th ser., 42, pp. 139-145, Aug. 1916.

of the water, second, a repression of the solubility of the phosphate formed. The starting point was a solution of one gram of di-calcium phosphate dissolved in just enough dilute hydrochloric acid. It was later found that the same result was obtained by mixing solutions of calcium chloride and of phosphoric acid in the correct proportions to form the di-calcium phosphate. This phosphate solution was then added to a nearly boiling solution of sodium chloride (150 gms. NaCl to 500 c.c.  $H_2O$ ). There was then added the precipitating agent (3.7 gms.  $UO_2(NO_3)_2 \cdot 6H_2O$  dissolved in a little water), which contained the necessary quantity of  $UO_3$  for the formation of the compound  $CaO \cdot 2UO_3 \cdot P_2O_5 \cdot 8H_2O$ . A small excess of uranium is not harmful. No precipitate should form at once. If the gradual addition of the uranium salt does cause an immediate precipitation, a little dilute hydrochloric acid is added to clear the solution before the addition of the bulk of the uranium salt. As this mixture slowly cools to room temperature yellow platy crystals of appreciable size appear.

That the degree of acidity is one of the factors controlling the size of crystals is shown in the formation of the sodium autunite. Crystals of the calcium variety were placed in a solution of sodium chloride to which hydrochloric acid was added in just sufficient quantity to dissolve these crystals. The acidity was then reduced by gradual addition of sodium carbonate dissolved in a little water to the point of re-precipitation. The volume of liquid was then increased to three liters by addition of water. As this volume of liquid stood for some three months exposed to slow evaporation at room temperature, crystals of sodium autunite were produced in size appreciably larger than in the early experiments. The clear liquid was decanted and the crystals washed free from sodium chloride. When examined under the microscope, they appeared wholly crystalline and homogeneous and showed well developed rectangular and 8-sided yellow plates similar to those of natural autunite.

An analysis of the air-dried crystals, obtained by "salting out" supposedly the calcium compound by the use of a sodium chloride brine, showed the somewhat surprising result that only about one-sixth the quantity of calcium belonging to autunite was present. The remaining five-sixth was sodium. Such a base exchange might have been expected, however, in view of the experience of Hille-

brand<sup>4</sup> who found that the calcium and potassium in the carnotites were mutually replaceable with ease.

#### ARTIFICIAL AUTUNITES PRODUCED

The crystals first obtained from a NaCl brine by the "salting out" process, had the following composition:

##### ANALYSIS OF THE CRYSTALS FROM NaCl BRINE.

	Per cent	Ratios
P <sub>2</sub> O <sub>5</sub>	16.13	.114 or 1
UO <sub>3</sub>	64.90	.227 or 2
CaO	1.10	.020
Na <sub>2</sub> O	5.62	.091
H <sub>2</sub> O (ign.)	13.22	.734 or 6.5
	100.97	

These ratios correspond closely to those required by the formula of autunite, after combining the sodium and calcium.

The  $\omega$  index<sup>5</sup> of this preparation is about 1.605, and  $\epsilon$  is not much lower, the birefringence being moderate. Most of the plates, averaging from about 0.01 to 0.05 mm. in width (and very much thinner) are isotropic on basal sections and uniaxial negative.

As the first object in this preparation of artificial autunites, was to make the calcium compound corresponding to the natural mineral, the unexpected result of obtaining sodium as an essential constituent was obviated, though still retaining a concentrated solution of a brine as "salting out" medium, by substituting calcium chloride (of a density of 1.25 or higher) for sodium chloride. The precipitation was repeated with the same proportion of calcium phosphate and uranium nitrate, and a similar well crystalized product was obtained. The well washed product, after being air dried for several days, gave the following results:

##### ANALYSIS OF THE CRYSTALS FROM CaCl<sub>2</sub> BRINE.

	Per cent	Ratios
P <sub>2</sub> O <sub>5</sub>	15.95	.112 or 1
UO <sub>3</sub>	63.00	.220 or 2
CaO	7.17	.128 or 1
H <sub>2</sub> O (ign.)	13.84	.769 or 6.7
	99.96	

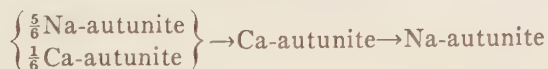
<sup>4</sup> Hillebrand, W. F., Carnotite and tyuyamunite and their ores in Colorado and Utah. *Amer. Jour. Science*, vol. 8, pp. 201-216, 1924, especially pp. 214-216; also earlier, same Journal, vol. 7, p. 439, 1913.

<sup>5</sup> All the optical determinations were made by W. T. Schaller.

The composition is the same as that of natural autunite, the ratios yielding the formula  $\text{CaO} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ . Optically, the material was very similar to natural autunite. The 4 and 8 sided plates were either isotropic or weakly birefracting with a characteristic gray-blue birefringent color. Twinning lamellae parallel to (100) are abundant.  $\omega$  is about 1.600 and  $\epsilon$  about 1.590, both being slightly variable. Another calcium product, obtained later by a similar process, gave uniaxial plates, containing 15.42 per cent  $\text{H}_2\text{O}$ , with  $\omega = 1.598$  and  $\epsilon$  about 1.586 and still a third similar product has the same  $\omega$  value.

A sample of this artificial calcium autunite was then digested with a solution of sodium chloride (about half saturated) on the steam bath for at least 2 days when the resultant product was found to be free from calcium and to contain much sodium. This product, with 16.09 per cent  $\text{H}_2\text{O}$ , consisted of uniaxial plates with  $\omega = 1.583$  and  $\epsilon = 1.566$ . Similarly, by starting out with a pure sodium compound and digesting it with a strong solution of calcium chloride, the sodium was replaced and the calcium compound again obtained.

As apparently the sodium and the calcium can replace each other with great ease, it seemed desirable to make a preparation of the sodium-autunite entirely free from calcium. As considerable material of the first made product—the  $5/6$  sodium,  $1/6$  calcium, with 5.62 per cent  $\text{Na}_2\text{O}$  and 1.10 per cent  $\text{CaO}$ —was available, a sample of it was first changed to the pure calcium-autunite. This was not analyzed quantitatively but only tested qualitatively. The isotropic plates had an  $\omega$  index of 1.601 and  $\epsilon$  index of  $1.588 \pm$ . This change to a calcium-autunite was made in order to verify the suspicion that sodium and calcium can replace each other in these compounds with great ease in either direction, the character of the brine used being the factor determining the composition of the product. A simpler method for the preparation of the pure sodium-autunite would have been to treat again the original product with a second  $\text{NaCl}$  brine. The calcium product obtained was then digested with  $\text{NaCl}$  brine and the calcium replaced by sodium. The sequence of formation of these three autunites can be expressed as follows:





Analysis of this end product, given below, showed that it represents the pure sodium-autunite, with the formula  $\text{Na}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ . In size, the plates average from about 0.05 to 0.10 m.m. across.

## ANALYSIS OF SODIUM-AUTUNITE.

	Per cent	Ratios
$\text{P}_2\text{O}_5$	16.00	.113 or 1
$\text{UO}_3$	64.51 by diff.	.224 or 2
$\text{CaO}$	None	.....
$\text{Na}_2\text{O}$	6.23	.101 or 1
$\text{H}_2\text{O}$ (ign.)	13.26	.737 or 6.5
	<hr/> 100.00	

Examined optically, most of the plates show a very slight birefringence.  $\omega = 1.582$  and  $\epsilon = 1.562$ .

One of the sodium-autunites prepared gave an anomalous result, in that while free from calcium, it contained an insufficient amount of sodium. There was no reason for suspecting such an anomalous result during its preparation. The 5/6 calcium, 1/6 sodium-autunite was used as a starting point. This was changed to the calcium-autunite which was then treated with a NaCl brine to change it to the sodium compound. The analysis showed a lower sodium content than previously obtained but also a higher water content.

## ANALYSIS OF ANOMALOUS SODIUM-AUTUNITE.

	Per cent	Ratios
$\text{P}_2\text{O}_5$	16.30	.115 or 1
$\text{UO}_3$	64.20	.223 or 2
$\text{CaO}$	None	<hr/>
$\text{Na}_2\text{O}$	3.96	.064 or 0.57
$\text{H}_2\text{O}$ (ign.)	15.88	.882 or 7.81
	<hr/> 100.34	

Optically, this sample did not differ from the sodium-autunite previously described except that many of the larger plates had an  $\omega$  index slightly higher than 1.580 and some of the smaller plates had an  $\omega$  index slightly under 1.580. The variation however was not greater than was observed in many of these preparations and it could not be definitely said that the preparation consisted of two

distinct compounds. There is a close approximation, in the ratios, to a compound of the type  $\frac{1}{2}\text{Na}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ , which is suggestive of the fact that Na and not  $\text{Na}_2$  replaces Ca. On the other hand, the water content being higher than in the sodium-autunite previously described, the preparation may be: (1) either a mixture of  $\text{Na}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  with  $\text{H}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , or (2) some water may function as  $\text{Na}_2\text{O}$  (or hydrogen as sodium), its formula can be written  $(\text{Na},\text{H})_2\text{O} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ . The previously described sodium-autunite with 6.23 per cent  $\text{Na}_2\text{O}$ , however, shows clearly the existence<sup>6</sup> of a compound with the formula  $\text{Na}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ .

The ease of base replacement so far encountered suggested that other bases might just as readily replace the sodium or the calcium. As a quantity of the sodium-autunite, containing 6.23 per cent  $\text{Na}_2\text{O}$  and corresponding to the formula  $\text{Na}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , was available this compound was used as a starting point for the preparation of the subsequent base-replacements. Using a solution of the chlorides of potassium, barium, manganese, copper, nickel, cobalt, and magnesium, the respective base replacement was easily effected and corresponding autunites prepared. Only lead was unsuccessful as a base replacement.

*Potassium.* By digesting the sodium autunite with a brine of KCl for several days, the crystals showed, by flame test, the presence of considerable potassium with only a negligible quantity of sodium. These crystals were not analyzed. The plates were 8-sided, and somewhat larger than usual with an average width of about 0.2 mm. Many of the larger plates are not rectangular in outline but have an angle of about  $82^\circ$  instead of  $90^\circ$  and seem to have been

<sup>6</sup> The composition of the anomalous sodium-autunite raises the question as to the replaceability of sodium and calcium. The preparation of the compound  $\text{Na}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , with 6.23 per cent  $\text{Na}_2\text{O}$ , shows that  $\text{Na}_2\text{O}$  can replace  $\text{CaO}$ , but the formation of the so-called anomalous sodium-autunite with only 3.96 per cent  $\text{Na}_2\text{O}$ , brings to attention the question as to whether or not one Na replaces one Ca, or expressed as oxides, one  $\text{Na}_2\text{O}$  may replace  $2\text{CaO}$ . Prof. Winchell has offered to undertake an X-ray investigation of these compounds and it is hoped that such a study may reveal relations that are pertinent to the question. The varying hydration is a factor that must be considered as the quantity of water held by the material is directly a function of the hygroscopicity of the surrounding air as well as a function of temperature. It is not practicable to continue the investigation in this laboratory and the problem is left open for anyone desirous of undertaking it.

changed to a modification that is not tetragonal, possibly related to bassettite. The plates show a fine rectangular grating structure, resembling microcline, and most of them give a negative uniaxial figure though some are biaxial with a variable but small axial angle.  $\omega$  is about 1.575 and  $\epsilon$  about 1.553.

*Barium.* Using a barium chloride brine, the resultant product contained 15.3 per cent BaO and 11.0 per cent H<sub>2</sub>O. The ratio of H<sub>2</sub>O to BaO is 6.1 to 1.0. These values for BaO and H<sub>2</sub>O are like those of the natural mineral uranocircite. Optically most of the plates are uniaxial, the basal plates showing many broad polysynthetic twinning lamellae after both (100) and (110).  $\omega$  is about 1.613 and  $\epsilon$  about 1.604.

*Manganese.* A manganese brine yielded a product which contained about 8 per cent MnO and 15 per cent H<sub>2</sub>O. Ratio of H<sub>2</sub>O to MnO = 7.6. Optically the plates show all the varieties described in the introduction. Most of the plates are broken up into a mosaic of irregular areas, some isotropic and others weakly birefracting. Some plates are biaxial with a moderately high birefringence. Some show the abnormal blue interference color. Diagonal twinning lamellae (after  $m(110)$ ) are abundant.  $\omega$  is about 1.60, varying from 1.598 to 1.601.

*Copper.* Treatment with copper chloride showed that copper readily enters into the mineral, the resultant product being decidedly greenish but complete replacement was not obtained, judging by the color and qualitative tests. As the copper compound is well known as a mineral, the experiment was repeated and the product partially analyzed. Its color was of a much deeper green color than the first product and evidently showed a greater replacement. The copper, nickel, and cobalt compounds were obtained by an overnight treatment on the steam bath in a covered beaker with the appropriate brine. As a result of the many experiments made, it seems desirable to let the product react with the brine for 2 or 3 days, in order to obtain complete replacement.

The copper compound, with  $\omega = 1.608$  on the average, but slightly variable, gave on analysis:

PARTIAL ANALYSIS OF COPPER-AUTUNITE.

	Per cent	Ratios
CuO	5.61	.070
Na <sub>2</sub> O	0.73	.012
H <sub>2</sub> O	15.62	.868 or 10.6

*Nickel and cobalt.* These two bases also readily replace the sodium at least to a considerable degree. The nickel product was of a greenish-yellow color and the cobalt of a pinkish brown.

*Lead.* Judging by the fact that lead functions as sodium in the minerals of the jarosite group, attempts were made to prepare a lead autunite by similar treatment of the sodium autunite with a lead brine. The resultant product was not homogeneous nor well crystallized and the lead content was 9 per cent above the theoretical value. However, a lead autunite was prepared by the method of slow precipitation and crystallization from a dilute solution. A solution of the mixed nitrates of uranium, calcium and lead was allowed to react slowly through a volume of 4 liters of water with a weak solution of phosphoric acid, (0.01 molar) which was more than enough to precipitate the bases.

All the salts were present in proper proportion to form calcium or lead autunite, with a 1:1 molecular ratio between the calcium and the lead. This arrangement was intended to permit a natural selection of base with respect to the calcium or the lead. After about two weeks the crystals obtained were washed free from soluble salts and analyzed for calcium and lead. Found, PbO, 19.5 per cent; CaO, none; H<sub>2</sub>O, 13.1; theory for lead, 20.6. Ratio of H<sub>2</sub>O to PbO = 8.4. The optical examination showed that much of the material was matted together into compact flakes of irregular shape, with some square plates. Many of the plates were slightly birefringent and biaxial. The material did not look as uniform or as perfect as the other preparations, or at least the individual crystals were not so perfect nor so freely developed. The  $\omega$  index is about 1.625.

Some of this lead-autunite was recrystallized by dissolving in a little HNO<sub>3</sub> and then neutralizing with CaCO<sub>3</sub> and letting the product slowly crystallize out after dilution to six liters. This product came out in well formed 8-sided plates, very weakly birefracting on the base and with an  $\omega$  index of 1.627.

*Magnesium.* Treatment with a magnesium chloride brine gave a product containing: MgO, 4.36 per cent; Na<sub>2</sub>O, trace; H<sub>2</sub>O, 15.74 per cent. Ratio of MgO:H<sub>2</sub>O = 8.1. The material is lighter colored than any of the other preparations. Optically the plates are either isotropic or weakly birefracting on the base. The  $\omega$  index is variable, with a mean value of about 1.58.



## SUMMARY

Artificial autunites were made by slow crystallization from dilute solutions and by a "salting out" process, using a chloride as the precipitating agent. Starting with sodium-autunite, and to a lesser degree with calcium-autunite, a series of base exchange autunites were prepared by treating the sodium-autunite with a strong solution of the chloride of the element which it was desired should replace the sodium. In this way, calcium, potassium, barium, manganese, copper, nickel, cobalt, lead, and magnesium autunites were easily prepared. Treating the sodium-autunite with a  $\text{CaCl}_2$  brine readily changed it to a calcium-autunite and treating the calcium-autunite with a  $\text{NaCl}$  brine readily changed it to the sodium-autunite. Apparently this change can be repeated alternately as often as desired.

Most of these autunites so prepared contain less than 8 molecules of water. Their refractive indices are summarized in the following table, the values being expressed as  $\omega$  and  $\epsilon$ , even though some of the products are biaxial and have the indices  $\gamma$ ,  $\beta$ , and  $\alpha$ . For these biaxial modifications,  $\gamma$  is represented by  $\omega$  and  $\beta$  is very close to  $\gamma(\omega)$ . The quantity of water present changes the indices appreciably, but no attempts were made to correlate the hydration of the substances with the humidity of the air, or to closely connect the indices with their water content.

REFRACTIVE INDICES OF VARIOUS ARTIFICIAL AUTUNITES.

Composition of exchange- able base	$\frac{5}{6}\text{Na},$ $\frac{1}{6}\text{Ca}$	Ca	Na	Anom- alous Na	K	Ba	Mn	Cu	Pb	Mg
Ratio of $\text{H}_2\text{O}$ to exchange- able base	6.5	6.7	6.5	7.8	—	6.1	7.6	10.6	8.4	8.1
$\omega$	1.605	1.600	1.582	1.580	1.575	1.613	1.60	1.608	1.625	1.58
$\epsilon$	—	1.590	1.562	—	1.553	1.604	—	—	—	—

As already stated in a footnote, the investigation can not be carried any further in this laboratory and the entire problem is open to anyone interested. In addition to the problem of base-replacement, there is the similar one of acid-replacement, for the  $\text{P}_2\text{O}_5$  can probably be replaced with  $\text{As}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$ , etc., with similar relative ease.

The ease of such base-replacement is a confirmation of earlier

work along similar lines, some of which was done many years ago. For example, Clarke and Steiger noted<sup>7</sup> the "easy replaceability of the soda in analcite" by ammonia and by silver oxide. Incidentally such equivalent functioning of  $\text{Na}_2\text{O}$ ,  $(\text{NH}_4)_2\text{O}$ , and  $\text{Ag}_2\text{O}$ , has been strikingly verified mineralogically by the later discovery of the minerals natrojarosite, ammoniojarosite, and argentojarosite.

<sup>7</sup> Clarke, F. W., and Steiger, George. The action of ammonium chloride upon silicates, *U. S. Geol. Survey Bull.* No. 207, 1902.

## PROCEEDINGS OF SOCIETIES

### PHILADELPHIA MINERALOGICAL SOCIETY

*Academy of Natural Sciences, May 2, 1929*

A stated meeting of the Philadelphia Mineralogical Society was held on the above date with the president, Mr. Trudell, in the chair. Sixty-five persons were present, including forty-three members.

Upon favorable recommendation of the council, the following were elected junior members: Messrs. Robert Bradley, Jack Semless, and Edward Wojtowicz. Mr. Cienkowski proposed the following for junior membership: Messrs. Randall Heiligman, Harry Eissler, Jr., and Richard Archibald.

Mr. F. B. Havens addressed the society on "*Symmetry in Crystals*." The historic development of the ideas of symmetry and the arrangement of points in space by Frankenheim, Bravais, Sohncke, Schoenflies, and Barlow were outlined. The derivation of the thirty-two classes of symmetry by diagraming the symmetry elements in stereographic projection was shown.

Messrs. Biernbaum and Cienkowski presented the plan for the proposed competitive exhibition of minerals by boys to be held on May 23rd at Northeast High School, prizes to be awarded at the meeting of the society in June.

SAMUEL G. GORDON, *Secretary*

### NEW YORK MINERALOGICAL CLUB

*Minutes of the April Meeting*

A regular monthly meeting of the New York Mineralogical Club, attended by forty-one members, was held at the American Museum of Natural History on the evening of April 17, 1929, with President Herbert P. Whitlock in the chair.

Dr. Albert Bardes, of New York City, and Mr. W. N. Berkely, of Yonkers, N. Y., were elected to membership.

The present officers were re-elected for another year, namely:

President	Herbert P. Whitlock
1st Vice President	Frederick I. Allen
2nd Vice President	George E. Ashby
Treasurer	Gilman S. Stanton
Secretary	Horace R. Blank

Dr. Benjamin L. Miller, of Lehigh University, addressed the Club on "*The Formation of the Primary and Secondary Limestone Minerals*." Bacteria and blue-green algae are believed to play an important part in the chemical precipitation of calcium carbonate from sea water. Dolomite is probably formed by the substitution of the calcium by magnesium derived either from sea water or from circulating ground waters. There is evidence that dolomitization can take place either before or after burial of the strata.

The secondary changes in limestones may be brought about by the circulation of cold meteoric waters or by heated waters accompanying compression and regional metamorphism. Among the products of the former process are calcite, flint nodules, and segregations of iron, manganese, lead, and zinc ores. The heated waters cause

the formation of muscovite and sericite from impure limestones. Wollastonite, garnet, magnetite, epidote, and graphite are formed by a greater degree of metamorphism. In contact metamorphism some of the material for the formation of new minerals is supplied by the igneous rock.

Mr. Radu demonstrated the phosphorescence of a synthetic ruby after exposure to ultra-violet light, by means of a new device permitting the detection of a very short period of phosphorescence.

Mr. Weidhaas exhibited chalcedony from Tampa and Biscayne Bays, Florida.

HORACE R. BLANK, *Secretary*

## REVIEWS

THE PHYSICS OF CRYSTALS. ABRAM F. JOFFÉ. Edited by Leonard B. Loeb. XI+198 pages, 61 figures. McGraw-Hill Book Co., *New York*. 1928.

Dr. Joffé presents in this book a series of lectures given at the University of California and edited by L. B. Loeb, Professor of Physics at California. Although the subject matter is clearly designed for the technical physicist yet there are many valuable crumbs for the mineralogist and geologist.

The lectures include a liberal amount of discussion of experimental work which has been done during the last twenty-five years by the author and his collaborators. The experiments include various types of deformation of crystals and the detailed study of results especially by the X-ray method. The analysis of these results is of exceptional interest to the geologist with its bearing on geologic stresses as expressed in the formation of schist minerals, minerals growing in fractures and their strength, etc. I recommend to any mineralogist the following four chapters: The elastic after effect; The elastic limit; The mechanism of plastic deformation; Strength.

The last part of the book is somewhat mathematical and deals with a phase of crystal physics which is still in advance of most of our application. It includes the electrical and associated effects which ultimately must command our attention but which most of us are still willing to see further advanced by the physicist before we can hope for any large degree of successful application.

The book is worthy of our most serious attention. It covers a phase of the subject that the mineralogist is seldom qualified to enter, but one that he cannot afford to neglect.

R. C. EMMONS

EINFÜHRUNG IN DIE KRISTALLSTRUKTURLEHRE. FERDINAND VON WOLFF. 169 pages, 119 figures. Quelle & Meyer, Leipzig. 1928.

This book according to the title is an introduction to the study of crystal structure. More properly speaking it is a synopsis of the entire field of crystal structure. To the mineralogist, however, who does not want to study the details of crystal structure analysis, it supplies a long-felt need.

The illustrations, so important in this science, are especially well chosen and unusually clear. The binding and printing of the volume are very good. Chapter I (16 pages) deals with the 32 crystal classes. It assumes that the student is familiar with crystallography. Since this cannot be expected of chemists, metallurgists, and others, the author could have dwelt at greater length on this subject. Chapter II



(34 pages) gives a good account of the 230 space groups and the 14 Bravais lattices, but the author omits almost entirely the point groups and their relationship to the lattices and space groups. Chapters III and IV contain very short discussions on the theory and production of X-rays and X-ray diffraction. The methods of crystal analysis are described in a few pages. This brevity is rather serious as whole paragraphs become unintelligible to the reader unless he has become familiar with the methods elsewhere. In Chapter V we read of the properties of the elements and the structures of atoms. The next two chapters occupy 50 pages and deal with the various crystal structure types thus far discovered. They follow very closely V. M. Goldschmidt's classification and discussion of structure types and atomic and ionic radii. Even the structure of olivine is included, but no account is given of any organic crystals. The last chapter takes up isomorphism, morphotropism, polymorphism, etc. A bibliography for the years 1924 to 1927 concludes the book. Unfortunately an alphabetical index was omitted which detracts from the value of the volume. Several typographical errors were noticed in the last third of the book.

JOHN W. GRUNER

NEUE MIKROSKOPISCHE BEOBACHTUNGEN AM CUBANIT (CHALMERSIT) UND ÜBERLEGUNGEN ÜBER SEINE LAGERSTÄTTENKUNDLICHE STELLUNG. PAUL RAMDOHR. *Zeitsch. f. praktische Geol.*, vol. 36, 1928, pp. 169-178.

A great deal of information including a complete bibliography on cubanite may be found in this paper. The author himself studied 32 occurrences of cubanite and finds that the mineral once considered as rare is very common in pyrrhotite-chalcopyrite ores, though he cannot explain its absence in many ores of apparently the same type. The crystallographic orientation of cubanite lamellae in chalcopyrite is carefully described. Its optical properties including pleochroism and behavior in reflected polarized light are given. The name cubanite (chalmersite) seems to include two minerals which the author calls cubanite 1 and cubanite 2. The latter seems to be a decomposition product of cubanite 1, which appears to be the true cubanite. Cubanite 2 can be distinguished from cubanite 1 by optical tests and then only by very careful study since they appear almost identical. In polarized light cubanite 2 is darker brown ("lederbraun") than cubanite 1 and remains this color on rotation of the stage, while cubanite 1 shows considerable anisotropism.

Cubanite seems to be confined to deposits formed at high temperatures, an observation in complete agreement with G. M. Schwartz's experiments (*Econ. Geol.*, vol. 22, 1927, p. 44). The occurrence of peculiar little stars (skeleton crystals) of sphalerite in chalcopyrite and cubanite is described.

JOHN W. GRUNER

#### NOTES AND NEWS

Dr. E. L. Bruce, professor of Mineralogy at Queen's University since 1920, has been appointed first Miller Memorial Professor of Research at Queen's University. The new chair has been founded by friends and students of the late Dr. Miller and by mining companies in northern Canada.

Professor J. E. Hawley, of the University of Wisconsin, has been appointed head of the department of Mineralogy at Queen's University. He is a graduate of Queen's University and succeeds Professor E. L. Bruce.



At the annual meeting of the Boston Society of Natural History the announcement was made that the "Walker Prize in Natural History," which was offered this year for the best paper submitted on any subject in the field of geology or mineralogy, was awarded to Dr. M. W. Senstius, of the department of geology of Rutgers University, for a memoir entitled "Studies in Weathering and Soil Formation in Tropical High Altitudes."

Amherst College has announced plans for its fifteenth geological and mineralogical expedition to the western area of the United States, under the direction of Professor Frederic B. Loomis.

Dr. H. von Philipsborn has been called to the Bergakademie at Freiberg in Saxony as successor to Dr. Kolbeck and Dr. K. Spangenberg succeeds Professor L. Milch at the University of Breslau.

Dr. Joseph L. Gillson, associate professor in the department of geology of the Massachusetts Institute of Technology, has been granted a leave of absence for the year 1929-1930, and will serve as associate professor of economic geology at Northwestern University.

Of the present officers of the Mineralogical Society of America both the secretary and treasurer will attend the International Geological Congress which will meet at Pretoria, South Africa, July 29-August 7, 1929.

Dr. F. J. Becke, emeritus professor at the University of Vienna, has been awarded the Wollaston medal of the Geological Society of London for his investigations on the crystalline schists.

Dr. J. Beckenkamp, professor of Mineralogy and Crystallography, has retired from active teaching at the University of Würzburg.

Dr. A. Bevan, assistant professor of Geology at the University of Illinois, has been appointed State geologist of Virginia.

Dr. H. A. Brouwer of the Techn. Hochschule at Delft has been appointed Director of the newly established Geological-Mineralogical Institute at the University of Amsterdam. He will also have charge of general Geology and Petrography.

Dr. Tom Barth of the University of Leipzig is spending a year at Harvard University, having received an appointment of Fellow of the International Education Board.

